

Optical Thin Film Technology: Mechanical Properties

Introduction

Functional optical coatings are used in applications such as reflection reduction (Anti-Reflection), color separation (image projectors, cameras), spectral bandpass filtering (medical, environmental diagnosis and monitoring), high reflection (mirror), and other specialized applications. These coatings are composed of thin layers of alternating high- and low-index materials, and their spectral operating ranges are determined by the optical properties, refractive index and absorption, of their composite layers. The physical and chemical natures of the thin-film layers as they are condensed and grow into solid films are determined by the deposition conditions.

The technology for film deposition needs to consider the mechanical and environmental conditions under which the micrometer-thin coatings must survive and function. Common examples of coatings that require high-durability are eye glasses, automobile windscreens, aircraft canopies, and other windows deployed in harsh environments that include high-velocity rain and sand erosion. The durability of coatings to various abrasive and chemical agents is determined to some degree by the chemical composition of the layers, but primarily by their cohesive and adhesive strengths and hardness, which are functions of the deposition process. Durability to mechanical forces is influenced by the nature of the microstructural growth of the lay-

ers during their condensation on the substrate surface. That microstructure, in turn, determines the magnitude and sign of the residual stress built into the thin-film multi-layer / substrate system. CMN V14, Issue 3 (Sept 2004) presented a structure zone model of film growth as affected by deposition energy.

Stress Compensation Techniques for Oxide-Compound Coatings

In this section, we expand on previous discussions and introduce techniques for achieving a balance or neutralization between tensile and compressive stresses. Background discussions about stress in coatings can be found in previous CMN issues: V15, Issue 2 (June 2005), which discusses the origins of intrinsic stress in film layers, and V16, Issue 2 (June 2006) which is concerned with development of stress during the growth stages.

To review, with tensile stresses the forces lie in the plane of the film / substrate, and left unchecked can cause thin substrates to bend from planar to concave shape or upon release of the tensile stress, cause the film to contract into "mud flat" cracks. Fluoride-compounds exhibit tensile stress, while Silicon dioxide (SiO_2) layers exhibit compressive stress with characteristic buckling due to expansive forces parallel to the substrate. In contrast, high-index oxide-compound films, especially sput-

tered refractory compounds, generally exhibit tensile stress properties. Thin substrates obtain a concave shape. Materials in the latter category include ZrO_2 , TiO_2 , HfO_2 , etc. But Nb_2O_5 , Ta_2O_5 and Al_2O_3 can be in either stress state depending on whether they are deposited by reactive evaporation or by sputtering.

Silicon dioxide is paired with one of the above high-index materials in optical coatings that function from UV wavelengths to >2 μm in the IR. The intent is to compensate the opposing forces and achieve a low- or zero-stress coating. Intrinsic stress forces accumulate with thickness, while extrinsic stresses increase with thermal expansion differences between the substrate and the coating. Intrinsic stresses are generated by the deposition process and the growth microstructure; these parameters are intimately related — as illustrated in the structure zone model referred to above. High deposition energy produces a densely packed small-scale microstructure that is also highly stressed. While films that grow in the environment of high-energy bombardment such as IAD and ion plating are physically hard and exhibit no water-induced optical changes, such films can exhibit adhesion failure, micro crack-caused scatter, brittleness, or substrate bending due to mechanical stresses.

Another more subtle effect of coating stress is the generation of stress-in-

duced birefringence. This is a problem for phase-sensitive optical components involved in interferometry, polarimetry, ultra-fast laser optics, and very narrow bandwidth filters such as used in telecom. The effects of coating-related stress can be detected by viewing between crossed polarizers. Colored fringes will be seen if the optic is mechanically distorted or the coating itself causes phase changes.

Technology has evolved to minimize stress and obtain and preserve the desirable mechanical and optical properties in multi-layer oxide-compound coatings. Some approaches are:

1. Selection of the appropriate deposition process (reactive e-beam, IAD, plasma assisted, ion plating, sputtering, etc),
2. Modification of process parameters (IAD energy, rate, deposition atmosphere and pressure),
3. Design of alternative material compositions (admixture, pre-processing),
4. Introducing stress compensation by design between layers and substrate, and
5. Post-deposition treatment.

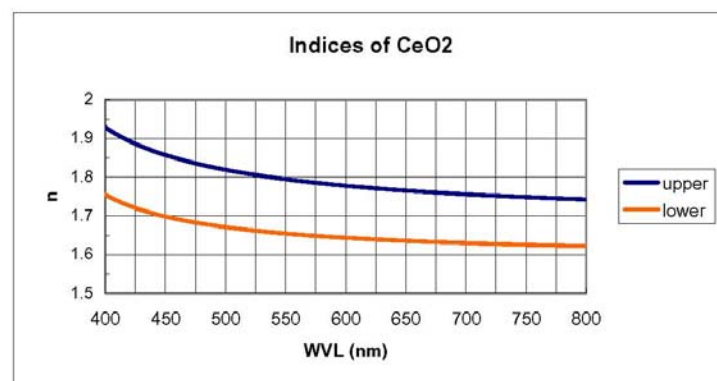
There are several ways toward approach 3. One is using “designed materials” based on the admixture of “foreign” materials with a host, a technique that we have discussed extensively in these issues, see for example CMN V17, Issue 1, March 2007 and older discussions of CERAC IRX™. In another method, co-evaporation or co-sputtering of high- and low-index materials is employed to compose a gradient between the two limits [1]. Alternating layers deposited lack a discrete interface and thus interface stress is also graded. An index gradient is also established. We have discussed techniques 1-3 previously; in this issue we emphasize the 4th and 5th technique.

In a typical multi-layer design consisting of quarter-wave optical thicknesses, the low-index layers (SiO_2) are physically thicker than the TiO_2 high-index layers. The stack will have net compressive stress if it is sputter deposited. The ability to substitute Nb_2O_5 for the high-index layer material can provide an immediate solution since sputtered niobia is tensile. Alternatively, annealing the SiO_2 / TiO_2 coating combination can increase the tensile stress and move the net stress toward a lower or possibly neutral value. Post-deposition in air at temperatures of 300-400° C for 2-4 hours is a typical annealing procedure. The actual time and temperature values to be used depend on the substrate material’s thermal expansion coefficient (e.g. glass vs. fused silica) and on the specific high-index material. Compensation can be achieved in some cases from the excess extrinsic tensile stress created in a coating that is deposited on a fused silica substrate when it is cooled to room temperature due to the low TCE of that substrate. Other effects of high-temperature post-deposition annealing are the removal of water from film pores and crystallization of layers, both events cause physical volume shrinkage and cause higher tensile stress. The growth of large micro-crystalline grain sizes common for the high-index materials can be thwarted in sputter deposition by interposing very thin layers of silica within thick high-n lay-

ers. In addition to increasing the packing density of the layer, optical scatter is reduced [2]. These benefits are also achieved by the use of mixed material evaporated by E-beam or sputtered [1]. Crystallization changes generally require post-deposition temperatures >500° C, and TCE differences can cause adhesion failure before the benefits of crystal size changes can be realized. Past CMNs have discussed the high-temperature transitions between anatase and rutile phases for titania, and phase changes in refractory materials such as zirconia that lead to inhomogeneous growth and refractive index variation with depth.

Film Growth Mechanics

Film growth microstructure is determined by the energetics of the arriving adatoms and the substrate surface condition onto which they condense to form a solid film. When the kinetic energy of the adatoms is low, they tend to initiate growth at randomly distributed, low-energy, point defect sites rather than grow with uniform area coverage as they would when surface mobility is high. Point defects can be residual polishing imperfection or micro-particulate ejection from the start-up of evaporation or sputtering. To understand the role of the surface energy, we refer again to the structure zone model. Island



growth produces film layers with large volume voids or low packing density. With some materials (predominately the high-index materials), nm-sized columns grow whose width tapers down as their height increases. Self-shadowing is responsible for this column shape. The structure has a volume density gradient that produces a refractive index gradient where the refractive index is higher near the substrate surface, consistent with the growth-gradient model.

An example of large index inhomogeneity is illustrated with a thick CeO₂ layer, and shown in the figure. Large distinct columns that contribute a large scattering component and low layer strength and hardness are observed for this coating. In some applications, this property can be used to advantage, but for general optical applications as we outlined in the introduction, high scatter and mechanical weakness are problematical. Process and composition variations can be used to reduce this inhomogeneity.

Materials that grow with packing densities less than that of the parent bulk, and this includes almost all pure oxide and fluoride compounds, exhibit changes in refractive index and mechanical stress as their films are alternately exposed to humid and arid conditions. Water vapor adsorbed on the surfaces of the growing columns in two components: a volatile and a permanent component. The volatile component responds to high and low humidity conditions, causing index and related optical performance changes. We have addressed two solutions. "Doped" materials such as CERAC IRX™ have reduced susceptibility to humidity changes because amorphous rather than microcrystalline columnar growth with high packing densities is produced. The packing density can be increased in Magnesium fluoride films

by depositing at high (300° C) substrate temperatures. With oxide compounds, high-energy processes such as IAD, ion plating, or sputtering are employed to compact the growth structure and produce moisture-stable films. As discussed above, these high-energy processes can create high stress unless the deposition parameters: pressure, energy, temperature and rate are optimized.

Used in combination with the added tool, post-deposition annealing, the optimum deposition process for a particular coating job can be developed.

References

1. B. J. Pond, J. I. Decker, C. K. Carniglia, and T. Raj, Appl. Opt. V28 No 14, 2800 (1989).
2. US Patent 5,930,046, July 27 1999. S. E. Solberg, and B. J. Pond.

New Data Sheets Available On-Line

Visit the Technical Publications page at www.cerac.com for newly revised product data sheets on the following CERAC materials:

AZO	YbF ₃
HfO ₂	YF ₃
LaTiO ₃	CIROM-2 ZnS
SiO ₂	ZnSe
Ta ₂ O ₅	ZrO ₂
Ti-oxides	

CERAC Coating Materials News is a quarterly publication of CERAC, inc.
A subsidiary of Williams Advanced Materials Inc.
P.O. Box 1178
Milwaukee, WI 53201-1178
Phone: 414-289-9800
FAX: 414-289-9805
web: www.cerac.com
e-mail: ceracinfo@beminc.com

Editor:
David Sanchez
 Sr. Materials & Applications Scientist
 CERAC, inc.

Principal Contributor:
Samuel Pellicori
 Pellicori Optical Consulting
 P.O. Box 60723
 Santa Barbara, CA 93160
 Phone/FAX: 805-682-1922
 e-mail: pellopt@cox.net

For a free subscription to CMN, please E-mail your name and address to ceracmarketing@beminc.com or send us a fax at 414-289-9805. Guest articles or topic suggestions are welcome.

*An electronic version of this publication can be accessed from the **Technical Publications** page of the CERAC web site at www.cerac.com. From there, link to the CMN Archives to view back issues.*

©Copyright 2007, CERAC, inc.

Coating Materials News

CERACTM
Incorporated

P.O.Box 1178
Milwaukee, WI 53201-1178
USA

PRSR STD
U. S. POSTAGE
PAID
MILWAUKEE, WI
PERMIT NO. 2418

C M N

Visit us at the Following Upcoming Trade Shows

- Vacuum Technology & Coating Expo, Milan Italy, Oct. 3-6 (Exhibiting company is G. Gambetti Kenologia, CERAC/WAM Rep)
- Photonex, UK, Oct. 17-18, UK (Exhibiting company is P&T Consulting, CERAC/WAM Rep)
- Night Vision, Washington, DC, Oct. 30-31
- MMM (Magnetism and Magnetic Materials) Tampa, FL, Nov. 5-9,
- MRS (Materials Research Society), Boston, MA, Nov. 27-29

Energize Your Thin Film Solar Cells

Advanced Inorganic Materials from CERAC

High Purity Powders and Sputtering Targets

- CIGS
- CdTe
- CdS
- Metals/Alloys (Al, Ag, Au, Ni, Pt, etc.)
- III-V Materials



Rare TCO Development

- ZnO Compositions
- Sb₂O₃ Mixtures
- In₂O₃ Mixtures



- Fully Characterized Materials
- Product Development and Customization
- Global Service and Technical Support

CERACTM
Incorporated

A subsidiary of Williams Advanced Materials Inc.
www.cerac.com
ceracinfo@beminc.com
414-289-9800 FAX: 414-289-9805